Study of chloride penetration in self-compacting concrete by simulation of tidal zone

K. Audenaert & G. De Schutter

Magnel Laboratory for Concrete Research, Department of Structural Engineering, Ghent University, Ghent, Belgium

ABSTRACT: By cyclic wetting and drying of concrete in the tidal zone, chloride ions are penetrating rapidly under the combined action of capillary suction of seawater followed by diffusion of chloride ions. In order to study this behaviour, a test set-up was used immersing specimens in a chloride containing solution, followed by a drying period. After distinct test durations the penetration depth is determined.

This test method was applied in the framework of a project studying the durability of Self-Compacting Concrete (SCC), including an experimental program on 16 SCC and 4 traditional mixes. Four types of cement and three types of filler are implemented and the influence of the amount of powder, the water/cement ratio and the cement/powder ratio is studied.

The influence of the combined action of capillary absorption and chloride diffusion on the penetration is investigated and a simplified model is proposed, leading to an accurate prediction.

1 INTRODUCTION

Chloride induced reinforcement corrosion is the main durability problem for concrete structures in a marine environment. If the chlorides reach the reinforcement steel, it will depassivate and start to corrode in presence of air and water. Since the corrosion products have a larger volume than the initial components, concrete stresses are induced, leading to spalling and degradation of the concrete structures. The most common transport mechanisms determining the chloride penetration velocity are diffusion (chloride gradients in standing water), capillary suction (chlorides transported with moving water) and permeation (chlorides transported with water under pressure). All three transport mechanisms may occur simultaneously.

The chloride penetration in concrete is largest for the part of a structure in the tidal zone. This is experimentally noted and is explained as the combined action of capillary suction and diffusion. The chloride containing sea water is penetrating the concrete by capillary suction in the wetting period. Because capillary suction is a fast transport mechanism, the chloride ions are penetrating to a relatively high penetration depth. In the drying period, the water is evaporating from the concrete, leaving the chloride ions in the concrete. From there, the ions will diffuse into the concrete. In the following wetting period, new chlorides will be penetrating into the concrete together with the sea water by capillary suction. The continuously increasing amount of chloride ions at the penetration depth by capillary suction is creating a high concentration gradient over the remaining concrete. From this a high diffusion velocity is created. In this way, the penetration velocity of the chloride ions in the concrete is higher for the tidal zone than for example for the permanently immersed zone.

To simulate real chloride penetration conditions in a tidal zone, a test method was developed, immersing specimens in a solution containing chlorides and exposing the specimens to air. The specimens are cylindrical with a diameter of 230 mm and a height of 70 mm. Each cycle takes approximately 1 hour, 1/3 wetting and 2/3 drying. In this test a complex combination of diffusion, capillary suction, wetting and drying is created. After 6, 12, 18, 24, 30 and 36 weeks the specimens are broken and the penetration depth is determined with silver nitrate solution.

Self-compacting concrete (SCC) combines a high flowability and a high segregation resistance, obtained by a large amount of fine particles and the use of superplasticizers. As the concept of selfcompacting concrete is different from traditional concrete, changes in durability are to be expected. As part of a larger project studying the durability of self-compacting concrete, the chloride penetration in self-compacting concrete was investigated. An experimental program was carried out on 16 selfcompacting concrete mixes and 4 traditional concrete mixes. Four types of cement and three types of filler (fly ash and two types of limestone filler with a different grading curve) are implemented and the influence of the amount of powder, the water/cement ratio and the cement/powder ratio is studied.

The obtained chloride penetration profiles are analysed and the influence of different parameters in the concrete composition are investigated. A simplified model, based on capillary absorption tests and chloride migration tests, is proposed, leading to an accurate prediction.

2 EXPERIMENTAL PROGRAM

2.1 Test method

In Figure 1, a photo is shown of the testing device for cyclic testing. It was developed at the Magnel Laboratory for Concrete Research by De Belie et al. (2002) for testing the chemical degradation of concrete by acids. The testing device consists of horizontal rotating axes, immersing the cylindrical concrete specimens (with a diameter of 230 mm and a thickness of 70 mm) alternatively to wetting by immersing in a chloride solution, present in recipients, and drying to air. One cycle takes approximately 1 hour, 1/3 wetting and 2/3 drying. In the recipients 2 litres of a chloride solution of 3.5% in water is present, wetting the outer 5 cm of the specimens. In this way, each point of the outer circumference is submersed during 1/3 of the rotation time.

From each of the mixes described in the next paragraph, 6 cylindrical specimens were made and stored in a climate room at $20^{\circ}C \pm 2^{\circ}C$ and more than 90% R.H. At the age of 28 days, the specimens were mounted on the testing device. After 6 weeks the first specimen is taken from the apparatus and broken in 3 pieces. With the silver nitrate solution (Otsuki et al. 1992), the penetration depth is determined at the freshly split section. With one specimen,



Figure 1. Testing device for cyclic testing.

6 chloride penetration depths profiles are measured. After 12 weeks, the second specimen is taken from the apparatus and tested. The next 4 specimens are tested at 18, 24, 30 and 36 weeks.

2.2 Concrete composition

At the Magnel Laboratory for Concrete Research, 16 SCC and 4 TC were investigated. In the first 9 mixes, a constant amount of fine particles or powder (cement and filler) is considered: 600 kg/m3; as well as a constant amount of water, sand and gravel, respectively 165 kg/m³, 853 kg/m³ and 698 kg/m³. For all mixes, river gravel 4/14 and river sand 0/4 are used except for mix SCC16. In this mix, the river gravel was replaced by crushed limestone 2/7 and 7/14. Four types of cement (CEM I 42.5 R, CEM I 52.5, CEM III A 42.5 LA and CEM I 52.5 HSR) and three types of filler (fly ash and two limestone fillers: P2 and S, the last having a much finer grading) are used. In the next three mixes the amount of powder was varied: 500 kg/m³, 700 kg/m³ and 800 kg/m³ with the same water/cement ratio (W/C) and the same water/powder ratio (W/P). In the mixes SCC13, SCC14 and SCC15, the amount of water is varied with a constant amount of cement and powder. For the traditional concrete mixes, three types of cement are used and for one mix the W/C ratio is varied by a different amount of cement.

The amount of superplasticizer was determined in order to obtain a suitable flowability without segregation. Also the flowing time in the V-funnel was measured (values between 5s and 10s), air content (values between 1% and 3%) and the U-box requiring self levelling. In Table 1, the mix composition is given together with the compressive strength at 28 days measured on concrete cubes with side 150 mm. Also the experimental and calculated values for H, describing the chloride penetration rate as explained in section 2.3, is given in Table 1.

2.3 Analysis of test results

In this type of test, a real situation is simulated, consisting of wetting and drying cycles. The chlorides are penetrating by diffusion and capillary absorption.

This makes it very complicated to model the test results. An example of the chloride penetration profile of SCC2 is given in Figure 2 and the regression curve is given in Figure 3.

The diffusion of chloride in concrete is following Ficks second law and can be written as:

$$C_x = C_o \left(1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right)$$
(1)

compr. strength [MPa]	57.3	68.0	66.1	70.1	56.9	66.2	46.5	64.2	68.7	60.1	55.9	50.9	68.7	46.6	40.3	73.3	48.6	49.7	53.7	50.2
Hcalc [mm/ √week]	2.9	2.7	2.7	2.9	2.9	2.0	3.2	2.7	2.3	2.3	3.4	3.8	2.1	3.7	4.0	2.9	2.9	2.9	2.7	2.7
Hexp [mm/ \/week]	3.0	2.5	2.2	2.6	2.9	2.0	3.9	2.4	2.1	2.7	3.2	3.6	2.2	3.5	4.1	2.7	3.8	3.7	2.8	2.8
C/P [-]	0.60	0.60	0.60	0.60	0.60	0.60	0.50	0.67	0.75	0.60	0.57	0.56	0.60	0.60	0.60	0.60	1.00	1.00	1.00	1.00
W/C [-]	0.46	0.46	0.46	0.46	0.46	0.46	0.55	0.41	0.37	0.46	0.48	0.49	0.40	0.55	0.60	0.46	0.46	0.46	0.41	0.46
glenium 51 [l/m³]	2.3	2.5	2.3	2.2	2.8	2.8	2.2	2.9	3.0	3.4	2.6	2.7	3.6	1.8	2.0	3.6				
gravel 2/14 [kg/m ³]																734				
gravel 4/14 [kg/m ³]	869	698	698	698	698	698	869	698	698	755	640	583	707	683	675		1225	1225	1200	1225
sand 0/5 [kg/m ³]	853	853	853	853	853	853	853	853	853	923	782	712	865	835	825	816	640	640	626	640
water [kg/m³]	165	165	165	165	165	165	165	165	165	137	192	220	144	198	216	165	165	165	165	165
fly ash [kg/m³]						240														
limestone filler P2	240	240	240	240			300	200	150	200	300	350	240	240	240	240				
limestone filler S [kg/m³]					240															
CEM I 52.5 HSR [kg/m ³]				360																360
CEM III A 42.5 LA [kg/m³]			360															360		
CEM I 52.5 [kg/m ³]		360																		
CEM I 42.5 R [kg/m ³]	360				360	360	300	400	450	300	400	450	360	360	360	360	360		400	
	SCC1	SCC2	SCC3	SCC4	SCC5	SCC6	SCC7	SCC8	SCC9	SCC10	SCC11	SCC12	SCC13	SCC14	SCC15	SCC16	TC1	TC2	TC3	TC4

Table 1. Concrete composition and compressive strength.



Figure 2. Chloride profiles of SCC 2.



Figure 3. Chloride penetration depth in function of time (SCC2).

with C_x = chloride concentration in the concrete at a distance x from the surface; C_o = surface chloride concentration; D = the diffusion coefficient, in this formula considered constant, and t = the time. This equation can also be written as:

$$x_{\rm dif} = 2\sqrt{D}\,{\rm erf}^{-1} \left(1 - \frac{C_x}{C_o}\right)\sqrt{t} = A\sqrt{t}$$
(2)

If the penetration depth is determined with silver nitrate, C_x will be a constant (0.07 N), and thus A will be a constant.

Also water absorption by capillary action during short time periods can be modelled by this kind of equation (Audenaert et al. 2003a, Reda Taha et al. 2001, CEB-FIB Model Code 1990):

$$x_{\rm cap} = S\sqrt{t} \tag{3}$$

with x = the penetration depth of the water, t = time and S = a capillary suction coefficient.

A first rough approximation of combined diffusion and capillary absorption is to take both coefficients *A* (in Equation 2) and *S* (in Equation 3) into one:

$$x_{\rm tot} = x_{\rm cap} + x_{\rm dif} = H\sqrt{t} \tag{4}$$

Using this test method, it is impossible to determine A and S separately. Therefore H is proposed to model the test results and is determined based on regression. For all concrete mixes, this regression value was determined and is given in Figure 4 and Table 1.

2.3.1 Cement type

Concrete with cement of a higher strength class (SCC2) has a denser pore structure resulting in a lower H-value. For a blast furnace slag cement (SCC3), both the chloride diffusion coefficient and the capillary suction coefficient will be smaller than for Portland cement (Neville 1994; Audenaert & De Schutter 2003b). Also the regression value for the cyclic test is smaller for SCC3 in comparison with SCC1. The fourth SCC is made with CEM I 52.5 HSR, which has a lower C_3A content. This C_3A is binding the chloride ions, forming calcium chloroaluminate (Neville 1994). Using this cement leads to a higher chloride penetration depth in comparison with SCC2, having the same strength class.

2.3.2 *Type of filler and aggregate (Figure 5)*

If a limestone filler with a finer grading is used (SCC5), the diffusion coefficient and the capillary suction coefficient are going to decrease a little due to the refining of the pore structure. H is also decreasing



Figure 4. Experimental and calculated values for H.



Figure 5. Influence of type of filler and aggregate.

a little. The fly ash (SCC6) gives a diffusion coefficient that is much lower (Audenaert & De Schutter 2003b). Also H is lower.

Using a crushed limestone as coarse aggregate (SCC16), results in a better bonding between paste and aggregates leading to a somewhat lower value for H.

2.3.3 Amount of cement (Figure 6)

If the amount of cement, with a constant amount of powder and water, increases (and the W/C ratio decreases for the same W/P ratio), both the diffusion coefficient and the capillary suction coefficient are decreasing. This results in a decreasing value for H, as illustrated in Figure 6.

2.3.4 Amount of powder

Increasing the amount of powder with a constant W/C and W/P leads to a higher amount of paste. However this paste has the same pore structure, causing no significant difference in H.

2.3.5 Amount of water (Figure 7)

Increasing the amount of water at constant C and P, leads to an increasing W/C and W/P ratio. Both the diffusion coefficient and the capillary suction coefficient will increase. This results in an increasing value for H.



Figure 6. Influence of amount of cement.



Figure 7. Influence of amount of water.

2.3.6 Traditional concrete

The values for H are much higher for TC than for SCC. Using a blast furnace slag cement (TC2) or CEM I 52.5 HSR (TC4) results in a lower value for H. A higher amount of cement with the same amount of water (TC3) results in a lower W/C and a lower value for H.

2.3.7 Conclusions

The penetration depth in real conditions is strongly influenced by the water/cement and water/(cement + filler) ratios. Decreasing one of these ratios or both is leading to a decreasing penetration depth. Another important conclusion is that the chloride penetration depth in SCC by cyclic immersion is lower than the penetration depth in TC.

3 MODELLING

3.1 Capillary absorption

Tests were carried out on the 20 concrete mixes in order to describe the capillary absorption behaviour. The mass increase and the height of capillary rise were determined during one week. A description of these tests, a discussion of the test results and the modelling of the capillary absorption behaviour in function of the capillary porosity is given in (Audenaert 2006; Audenaert et al. 2007). With this model, the penetration depth after 20 minutes, x_{cap} , is calculated and given in Table 2.

In order to understand the influence of wetting and drying, additional tests were carried out on 3 concrete cubes of the 20 mixes. The cubes were immersed in water for 24 hours and than left to dry out during 24 hours ($20 \pm 3^{\circ}$ C, 60 ± 3 R.H.), followed by a new cycle of wetting and drying. Each time, the concrete mass was measured. The same was done for 3 other cubes, which were immersed one week in water, followed by 1 week of drying ($20 \pm 3^{\circ}$ C, 60 ± 3 R.H.). The mass was measured daily. For both types of cycles, the total mass increase after the first wetting period.

Based on these test results, it was supposed for the tests with cyclic exposure to chlorides that the height of capillary rise will never become larger than the height after the first wetting cycle.

In each wetting cycle the water, containing chlorides, will bring them into the concrete. During the drying cycle, the water will evaporate and the chlorides will remain in the concrete. Based on a literature review described in (Audenaert 2006), it was supposed that a chloride content of 0.55% of the mass of cement is present in the concrete at x_{cap} . This is a mean value for the whole duration of the test (36 weeks).

	x _{cap} (mm)	x _{dif} , 6 weeks (mm)	x _{dif} , 18 weeks (mm)	x _{dif} , 36 weeks (mm)	x _{tot} , 6 weeks (mm)	x _{tot} , 18 weeks (mm)	x _{tot} , 36 weeks (mm)
SCC1	2.1	4.7	10.2	15.5	6.8	12.2	17.6
SCC2	2.0	4.4	9.5	14.5	6.3	11.5	16.5
SCC3	1.9	4.4	9.5	14.5	6.3	11.5	16.5
SCC4	2.1	4.7	10.2	15.5	6.8	12.3	17.6
SCC5	1.9	4.3	9.4	14.3	6.2	11.3	16.2
SCC6	1.8	3.7	8.1	12.3	5.5	9.8	14.0
SCC7	2.1	4.7	10.2	15.5	6.8	12.2	17.6
SCC8	1.6	3.1	6.7	10.3	4.7	8.4	11.9
SCC9	2.3	5.1	11.1	16.9	7.4	13.4	19.2
SCC10	1.9	3.7	8.0	12.2	5.6	9.9	14.1
SCC11	2.3	5.6	12.1	18.4	7.9	14.4	20.8
SCC12	2.5	6.3	13.6	20.8	8.8	16.2	23.3
SCC13	1.7	3.4	7.3	11.2	5.1	9.0	12.9
SCC14	2.6	6.0	13.0	19.8	8.6	15.6	22.4
SCC15	2.9	6.5	14.1	21.5	9.4	17.0	24.5
SCC16	2.1	4.7	10.1	15.5	6.8	12.3	17.6
TC1	2.6	4.5	9.9	15.1	7.1	12.5	17.7
TC2	2.6	4.5	9.9	15.1	7.1	12.5	17.7
TC3	2.4	4.2	9.2	14.1	6.6	11.6	16.5
TC4	2.4	4.2	9.0	13.8	6.5	11.4	16.2

Table 2. Modelling results.

3.2 Diffusion

From the penetration depth of the capillary absorbed water, x_{cap} , the chloride ions will start to diffuse further into the concrete. This penetration depth was calculated with the next formula:

$$x_{\rm dif} = 2\sqrt{D} \, {\rm erf}^{-1} \left(1 - \frac{c_x}{c_0} \right) \sqrt{t}$$

A time dependent diffusion coefficient was taken into account, with m equal to 0.27:

$$D = D_{\text{ref}} t^{-m}$$

In order to determine the diffusion coefficient of the concrete mixes and the time dependent behaviour, non steady state migration tests were carried out following NT BUILD 492. At the age of 28 days, 2, 3, 6, 12 and 24 months the migration coefficient was determined. The diffusion coefficient was determined from the non-steady state migration coefficients following the method described in (Audenaert 2006, Tang 1996).

3.3 Modelling results

In Table 1 and Figure 4, the modelling results are given. A good correlation between the calculated and

the measured values is obtained, certainly for self compacting concrete.

4 CONCLUSIONS

An experimental program on 16 self-compacting concrete mixes and 4 traditional concrete mixes is carried out concerning the behaviour with respect to chlorides in a test simulating real conditions (wetting and drying, capillary suction and diffusion). Four types of cement and three types of filler (fly ash and two types of limestone filler with a different grading curve) are used and the influence of the amount of powder and water, the water/cement ratio and the cement/powder ratio is studied.

Based on these tests, the conclusion is that the penetration depth in real conditions is strongly influenced by the water/cement and water/(cement+filler) ratios. Decreasing one of these ratios or both is leading to a decreasing penetration depth. Another important conclusion is that the chloride penetration depth in SCC by cyclic immersion is lower than the penetration depth in TC.

The test results were modelled based on the capillary absorption behaviour and the diffusion process. A good agreement is obtained, certainly for self-compacting concrete.

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